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DIELECTRIC CONSTANT AND INTERATOMIC FORCES

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ABSTRACT. The existing classical theory of dielectric constant is improved by considering a more detailed form for the interatomic forces and the corresponding change in the polarisation of the medium. A procedure has been suggested to determine the net polarisation. The theory is finally tested by considering the low and high frequency dielectric constant data of alkali halide crystals.

INTRODUCTION

The mechanism of polarisation of a dielectric when placed in an electric field is now fairly well understood Debye (1929). In developing such a theory the problem is posed in the calculation of the effective field, E_{eff}, responsible for the polarisation of each of the atoms or molecules of the medium. Mott and Gurney (1948) discuss a procedure for evaluating E_{eff} in which the contribution arising from the polarisation due to the overlap of the neighbouring ions is also included. We follow the same general approach and reformulate the theory taking into account a more realistic force-field. We further specialize and confine our discussion to the alkali halide crystals having the sodium chloride type of structure. For such crystals the potential energy when considering only the nearest neighbour interaction is, [Kachhava and Saxena (1963)and Saxena and Kachhava (1964),]

$$\phi(r) = -\frac{e^2}{r} + a \exp(-r/\rho) - \frac{c}{r^6} - \frac{a}{r^8}. \tag{1}$$

Here r is the interionic separation, e the electronic charge, a and ρ are the potential parameters, and c and d are the van der Waals constants.

THEORY

If we represent the polarisation of the medium by P, when placed in an electric field of intensity E, the effective field responsible for polarising the molecule is given by

$$E_{eff} = E + \frac{4\pi}{3} P. \tag{2}$$

In many crystals, as in alkali halides, there is considerable overlap between the negative and adjacent positive ions. This causes a reduction in that part of the

effective field which is due to the polarisation of the medium. This necessitates writing equation (2) in the following form,

$$E_{eff} = E + \frac{4}{3}\pi P(1-\beta) = E + \frac{4}{3}\pi P\gamma. \qquad \ldots (3)$$

We further suggest that β or γ can be determined if $\phi(r)$ be known and for the particular form of equation (1) it is

$$\beta = 1-\gamma = \frac{\left(\frac{r_0}{\rho}\right) ae^{-r_0/\rho} - \frac{6c}{r_0^6} - \frac{8d}{r_0^8}}{e^2/r_0} \qquad \ldots (4)$$

Here r_0 is the equilibrium interionic separation. It may be remarked that $\gamma = 0 (\beta = 1)$ corresponds to maximum overlap and $\gamma = 1$ $(\beta = 0)$ to no overlap between the ions.

As shown by Mott and Gurney (1948) the high frequency dielectric constant, ϵ_0, is given by

$$\frac{\epsilon_0 - 1}{4\pi} = \frac{N(\alpha_1+\alpha_2) - (8/3)\pi N^2\alpha_1\alpha_2(1-\gamma)}{1 - (4/3)\pi N(\alpha_1+\alpha_2) + (16/9)\pi^2 N^2\alpha_1\alpha_2(1-\gamma^2)} \qquad (5)$$

in which N is the number of ion pairs per unit volume and α_1 and α_2 are the polarisabilities of the two ions.

Again following Mott and Gurney (1948) it can be shown that the low frequency dielectric constant, ϵ, is

$$\frac{\epsilon - 1}{3 + (\epsilon-1)\gamma} = \frac{\frac{4\pi}{3} N(\alpha_1+\alpha_2) - \frac{32}{9}\pi^2 N^2\alpha_1\alpha_2(1-\gamma)}{1 - \frac{4\pi}{3} N(\alpha_1+\alpha_2)(1-\gamma) + \frac{16}{9}\pi^2 N^2\alpha_1\alpha_2(1-\gamma)^2} + \frac{\frac{4\pi}{3}\delta}{1 - \frac{4\pi}{3}\delta(1-\gamma)}, \qquad (6)$$

in which $\delta = 2\frac{Ne^2}{p}$, where

$$p = 4\left[\omega''(r_0) + \frac{2}{r_0}\omega'(r_0)\right], \qquad \ldots (7)$$

and

$$\omega(r) = ae^{-r/\rho} - \frac{c}{r^6} - \frac{d}{r^8} \qquad \ldots (8)$$

A much cleaner and physical result is obtained by combining relations (5) and (6) when one gets

$$\frac{\epsilon-1}{3+(\epsilon-1)\gamma} = \frac{\epsilon_0-1}{3+(\epsilon_0-1)\gamma} + \frac{\frac{4\pi}{3}\delta}{1-\frac{4\pi}{3}\delta(1-\gamma)} \qquad \ldots (9)$$

RESULTS

We proceed to check the theory as represented by equations (5), (6) and (9) by considering alkali hlide crystals in particular. The potential parameters a and ρ were determined by writing equation (1) in the form

$$\Phi(r) = -\frac{\alpha e^2}{r} + Ge^{-r/\rho} - \frac{C}{r^6} - \frac{D}{r^8}, \qquad \ldots (10)$$

and using the Born-Mayer conditions viz.,

$$\frac{d\Phi(r)}{dr} = \frac{3VT}{NK}\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_P \text{ at } r = r_0, \qquad \ldots (11)$$

and

$$\frac{d^2\Phi(r)}{dr^2} = \frac{9V}{NK}F_{T,P}, \text{ also at } r = r_0 \qquad \ldots (12)$$

Here α is the Madelung constant, C and D are van der Waals constants and their values as given by Mayer (1933) are used, T the absolute temperature, $\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_P$ the coefficient of thermal expansion, $F_{T,P}$ is a factor involving $\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_P$, $K, \left(\frac{\partial K}{\partial P}\right)_T$ and $\left(\frac{\partial K}{\partial T}\right)_P$, P, V and K are the pressure, molar volume and the coefficient of compressibility respectively In the calculations described later the polarisability values wherever needed are those of Pauling (1927) Values of r_0, $K, \left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_P$, and $F_{T,P}$ as compiled by Saxena (1965) earlier are used.

In Table 1 we report the high frequency dielectric constant of alkali halide crystals. The experimental values are as listed in reference (2). Computed values of ϵ_0 are according to equation (5) with three different values of γ. These are $\gamma = 0$, and 1 being the two extreme values, and γ as calculated from equation (4). The latter γ values are also recorded in the Table I, column 2 It will be seen that ϵ_0 values are not much dependent on γ indicating thereby, as expected also, feeble dependence of ϵ_0 on the degree of overlapping between the ions. It is

interesting to note that in general there is a satisfactory agreement between theory and experiment.

In Table II we discuss the low frequency dielectric constant, ϵ, which is dependent on overlapping of the neighbouring ions in a much more pronounced fashion. This is substantiated by the computed values of c reported in the Table for the two extreme values of γ. The criteria of fixing γ thus is anticipated to have a crucial test in this case It is encouraging to note that the calculated values according to Equation (6) are in good agreement with the experimental values and specially when one recalls the rather large uncertainty associated with the computed values due to the greater uncertainty in the polarisability data. We personally regard this agreement as evidence of an overall adequacy of the theory of dielectric constant as well as of Equation (4).

A way out of avoiding the uncertainty creeping in the calculation of c based on Equation (6) is possible if one utilises the relation of Equation (9) We use this relation in conjunction with the experimental ϵ_0 and γ values to calculate c. These are also recorded in Table II, column 7. It is to be noted that the agreement in almost all cases is appreciably improved

The relation given by Equation (9) can also be utilised to fix the values of γ itself. In such a calculation experimental values of ϵ and ϵ_0 are used. The success of the procedure is therefore related to the accuracy with which these constants can be determined. The γ values obtained according to this procedure are recorded in Table I, column 3.

Within the scope of large uncertainty in the γ values obtained from Equation (9) we feel it reasonable to conclude that the two sets of γ values are in good agreement with each other, again lending confirmation to the procedure suggested for evaluating γ.

So far we have essentially worked within the framework of classical theory of dielectric constant as modified by Mott and Gurney (1948). In this picture the effective charge of the ions is assumed to be uneffected Szigeit (1949) presented a different theory by considering that overlap causes deformation of the electronic shells so that they are no more spherical, as usually assumed. This approach thus finally makes the reduction in polarization so far considered equivalent to a change in the value of the charge on the ions. According to this latter theory the actual charge ze on an ion behaves like having an effective value of sze. Szigeti (1949, 1950) has calculated the value of s for thirteen alkali halides and eleven of these are reproduced in Table III. If this theory is made equivalent to that of Mott and Gurney (1948) s and γ should be identifiable. We further confirm this by calculating ϵ_0 and c from Eqs. (5) and (9) respectively by using s values as listed in Table III for γ in them In this very Table in columns 3 and 5 we report these values and their percentage deviations from the corresponding experimental values in columns 4 and 6 respectively.

These values are seen to be in good agreement and also favourably compare with the findings of Table I and II. The low frequency dielectric constant c

TABLE I

Values of γ and ϵ_0 for alkali halide crystals

Crystal	Calculated γ values			ϵ_0			
				Calculated			
	Eq. (4)	Eq. (9)	Exptl.	γ variable	% dev.	$\gamma=0$	$\gamma=1$
LiF	0 74	0 49	1 92	2.13	+10 9	2.13	2.16
LiCl	0.68	0 46	2 75	3.53	+28.4	3 51	3.54
LiBr	0 70	0.51	3 16	3.83	+21 2	3 65	3 84
LiI	0 67	0 66	3 80	4.76	+25.3	4.75	4.78
NaF	0 70	0.36	1.74	1 77	+ 1 7	1 74	1.78
NaCl	0 70	0.70	2 25	2 67	+18 7	2.63	2 70
NaBr	0 70	0 21	2 62	2.90	+14 5	2 83	2.93
NaI	0.69	0 63	2 91	3 45	+16.5	3 31	3 48
KF	0.74	0.79	1.85	1 75	− 5 4	1.69	1.78
KCl	0 71	0.41	2 13	2 27	+ 6 7	2 16	2 31
KBr	0 69	0.49	2 33	2.42	+ 3.4	2.32	2 48
KI	0 70	0 30	2.69	2 78	+ 3 3	2 67	2 84
RbF	0 71	0 88	1.93	1 87	− 3 1	1 79	1 91
RbCl	0 71	0 64	2.19	2 23	+ 1 8	2.10	2.29
RbBr	0 69	0 84	2.33	2.34	+ 0 4	2.21	2.40
RbI	0 70	0.53	2 63	2 63	0 00	2 50	2 71

Av.Abs. % dev. 10 1

TABLE II

Experimental and calculated ϵ values for alkali halide crystals

Crystal	Exptl.	Calculated Eq (6)				Calculated Eq. (9)			
		γ variable	%dev	$\gamma=0$	$\gamma=1$	γ variable	%dev.	$\gamma=0$	$\gamma=1$
LiF	9.27	12 19	+31.5	6.45	20 3	10.50	+13 3	6 24	15.13
LiCl	11 05	14 14	+27.9	5 25	44.3	9.79	−11 4	5 49	17.35
LiBr	12 1	14.45	+19.4	5.03	66 8	10.66	−11.9	5 54	19.07
LiI	11.03	15.69	+42.2	6 76	67 2	11.13	+0 9	5 80	23.81
NaF	6.0	7 10	+18 3	5.19	9 64	7 03	+17.1	5 19	12 90
NaCl	5.62	7 84	+39 5	4.77	11.34	6 37	+13 3	4.36	8 31
NaBr	5 99	8 21	+44 5	4.85	12.49	7.27	+21 4	4 64	10 00
NaI	6 60	8 68	+31.5	4.98	13 80	7 03	+6 5	4 58	9 82
KF	6 05	5 44	−10.8	4 10	6 63	5 79	− 4 3	3.99	6.99
KCl	4.68	5.83	+24.6	3 98	7.54	5 46	+16.6	3.95	6.63
KBr	4 78	4.89	+ 2.3	3 90	7.46	4.47	− 6 5	3 96	6.83
KI	4 94	6 56	+32.4	3.26	8.99	6.23	+26 1	4 28	8 25
RbF	5.91	5.18	−12.3	3.84	6 29	5.23	−11 5	3.98	6 39
RbCl	5 0	5.12	+ 2 4	3.67	6.41	5 06	+ 1.2	3.76	6 04
RbBr	5.0	5 13	+2.6	3 70	6.57	5.16	+ 3 2	3 81	6.57
RbI	5 0	5.09	+13.8	3.84	7.20	5.57	11 4	3 97	6.82
Av. Abs. % dev.			22.2				11.2		

TABLE III

Calculated values of ϵ_0 and ϵ from Eqs (5) and (9) respectively using s values of Szigeti for γ

Crystal	s	Calculated ϵ_0	% dev	Calculated ϵ	% dev.
LiF	0.83	2.13	10 9	11.7	26 2
NaF	0 93	1 78	2.2	8 63	43 8
NaCl	0 74	2 68	19 1	6 57	15.1
NaBr	0 69	2.86	9 2	7 18	19 9
NaI	0 71	3 46	18 2	7 20	9 1
KCl	0 80	2 32	9.0	5 77	23 3
KBr	0 76	2 46	5.6	5 69	19.0
KI	0 69	2 75	2 2	6 28	27.1
RbCl	0 84	2 25	2 8	5 44	8 8
RbBr.	0 82	2.36	1 3	5.57	11.4
RbI	0 79	2.67	1 5	5.84	16 8
		Average % dev	7.5		19 9

now on thea verage is reproduced within a margin of 20 per cent. In Table II we find the reproduction to be relatively superior. The average absolute deviation was 11.2 per cent. This indicates a preference for the use of γ values as obtained here in the theory of Szigeti (1949) for s. These results further lend confirmation to the picture advanced here for the role played by the overlap forces in the dielectric polarisation.

APPENDIX A

While developing the theory of dielectric constant in this paper we have tried to take into account the effect of the overlap on the polarisation of the medium The reduction is estimated by introducing a factor β (or γ), which is defined by equation (4). This defining relation was stated more or less on an ad hoc basis and here we present a simple brief proof for the same.

In the absence of overlap the polarisation P of the medium is entirely due to charge-charge interaction. If the potential energy because of this interaction be ϕ_e we have

$$\phi_e = -\frac{e^2}{a}. \tag{A1}$$

If I_e is the corresponding intensity of the electrical field then the force, F_e, experienced by a charge q in the polarised medium is

$$F_e = qI_e = -\frac{\partial \phi_e}{\delta r} . \qquad \ldots \quad (A2)$$

In the presence of overlap the polarisation of the medium is altered, and so are the electrical intensity and the force on a charge. The force F_0 now acting on the same charge q because of the overlap only is

$$F_0 = qI_0 = -\frac{\partial \phi_0}{\partial r} . \qquad \ldots \quad (A3)$$

I_0 is that part of the total electrical intensity which owes its origin to the overlap force F_0. The defining relations for ϕ_0 for the potential of equation (1) is

$$\phi_0 = a \exp(-r/\rho) - \frac{c}{r^6} - \frac{d}{r^8} . \qquad \ldots \quad (A4)$$

Obviously

$$\beta = \frac{P_0}{P_c} = \frac{I_0}{I_e} = \frac{\partial \phi_0 / \delta r}{\partial \phi_e / \partial r} . \qquad \ldots \quad (A5)$$

or

$$\beta = 1 - \gamma = \frac{\left(\frac{r_0}{\rho}\right) a e^{-r_0/\rho} - \frac{6c}{r_0^6} - \frac{8d}{r_0^8}}{e^y / r_0} \qquad \ldots \quad (A6)$$

APPENDIX B

In the theory of the dielectric constant discussed in this paper the effect of overlap of the neighbouring ions is regarded to cause the reduction in the polarisation of the medium. In this picture the effective charge of the ions is assumed to be uneffected. Szigeti (1949, 1950) has considered this problem in a different way. He assumes that the reduction in the polarisation is equivalent to a change in the value of the charge on the ions. He introduces a parameters to estimate the refunction in the actual value of the charge. These two pictures can be regarded as equivalent and his s values can be compared with our values. The two sets of values agree reasonably well. Szigeti's ideas have been further developed (Dick *et al.*, 1958; Hanlon *et al.*, 1959) and some comments in this direction we hope to report in due course.

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